Publication number	H10(1998)-236826
Date of filing	February 25,1997
Applicant	SAKAI CHMICAL IND.

CLAIMS

[Claim(s)]

[Claim 1] The two-layered structure grain-like constituent, which has the main layer consisting of a lithium nickel multiple oxide and the surface layer consisting of a lithium cobalt multiple oxide. The cobalt/(nickel + cobalt) atomic ratio from the surface to 0.1 um in depth is 0.2 - 1.

[Claim 2] The two-layered structure grain-like constituent according to claim 1 that consists of a lithium nickel multiple oxide of the main layer expressed by general formula (I), $Li_pNi_{1-x}A_xO_y$ (wherein A is at least one sort of elements chosen out of B, Mg, Al, Si, Sc, Ti, V, Cr, Mn, Fe, Co, Cu, Zn, Ga, Y, Zr, Nb, Mo, Ru, Sn, Sb, La, Ce, Pr, Nb, Hf, Ta, and Pb, $0.90<=p<=1.10$, $0<=x<=0.25$. $1.825<=y<=2.3$)

[Claim 3] The two-layered structure grain-like constituent according to claim 1 that consists of a lithium nickel multiple oxide of the surface layer expressed by general formula (II), $Li_qCo_{1-a}Z_aO_b$ (wherein B is at least one sort of elements chosen out of B, Mg, Al, Si, Sc, Ti, V, Cr, Mn, Fe, Co, Cu, Zn, Ga, Y, Zr, Nb, Mo, Ru, Sn, Sb, La, Ce, Pr, Nb, Hf, Ta, and Pb, $0.90<=q<=1.10$, $0<=a<=0.25$. $1.825<=b<=2.3$).

[Claim 4] The two-layered structure grain-like constituent according to any of claim 1 - 3 is substantially spherical. Its mean particle diameter is 3-100 um and.

[Claim 5] The lithium ion secondary battery using-the two-layered structure grain-like constituents as a cathode active material according to any of claim 1 - 4.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[The purpose of this invention]

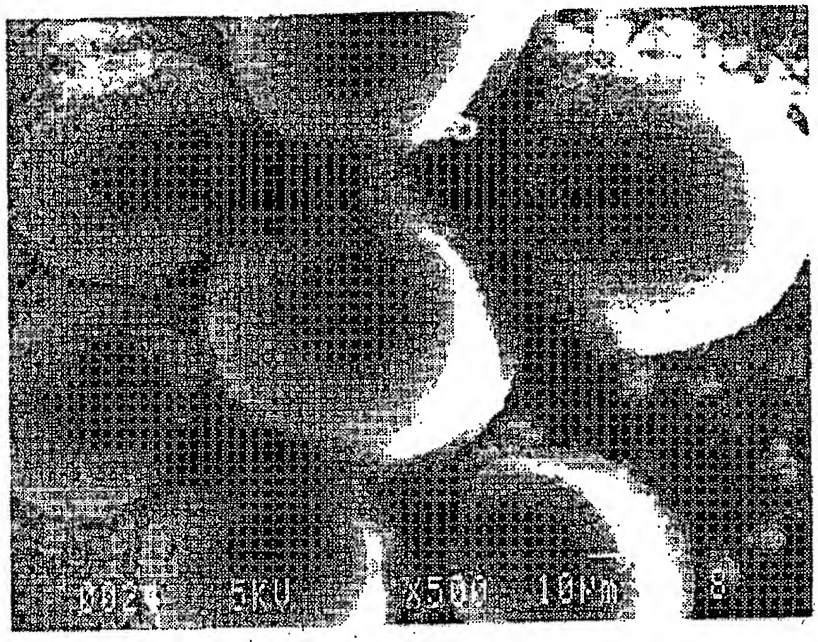
To improve safety issue. To offer the lithium ion secondary battery that has a good stability under elevate temperature and a high capacity.

[Example]

[Example 1]

[0043] Under ammonium-ion presence, sodium-hydroxide aqueous solution was added into nickel-nitrate aqueous solution continuously to neutralize. The secondary particle of nickel hydroxide consisting of the aggregated-particle was obtained. The specific surface area of this powder was 148m²/g. The SEM photograph of this powder is shown in drawing 2.

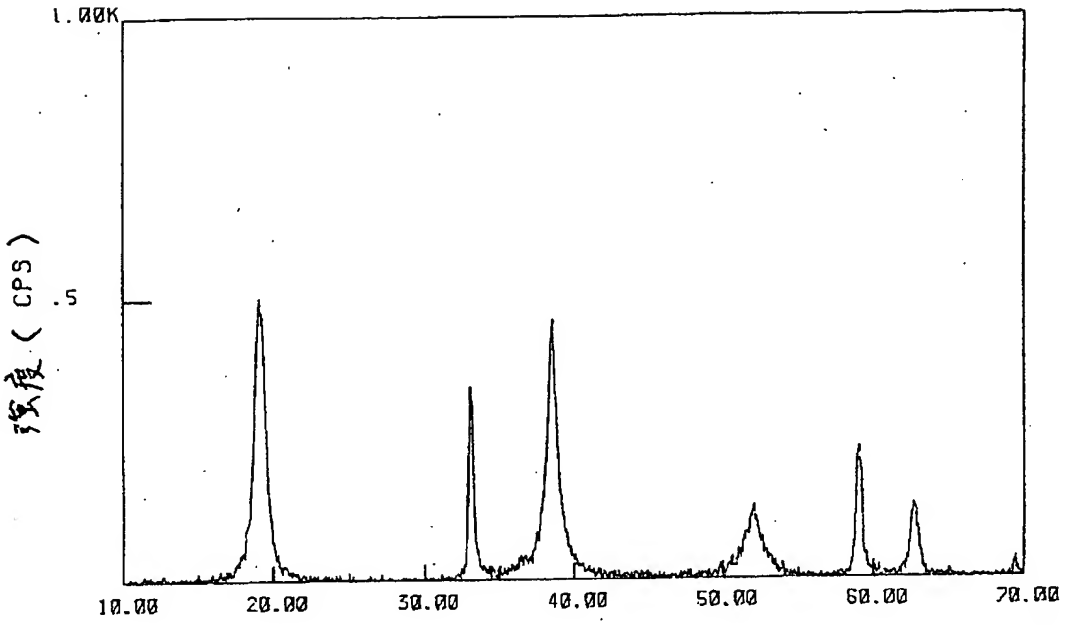
図面代用写真



2

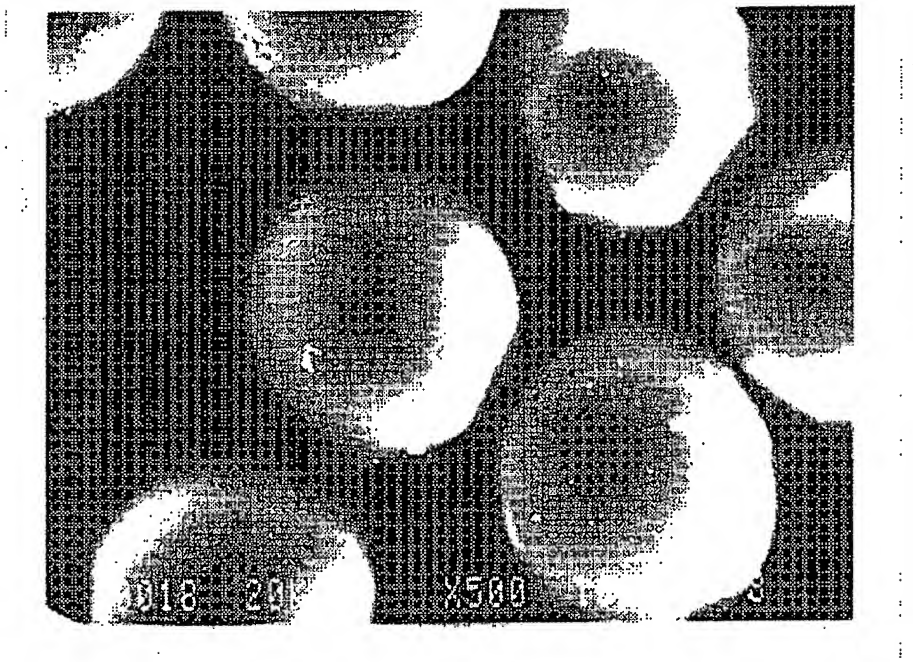
[0044] The slurry was obtained by dispersing this spherical nickel hydroxide 18.54g in water 0.1L. Cobalt-nitrate aqueous-solution (1.2 mol / L) 17.0mL was added to the slurry under being ammonium-ion, and the beaker was sealed. Nitrogen gas replacement in the beaker was carried out by introducing nitrogen gas into the slurry at the rate of 0.5L/min with stirring. 30 minutes after, sodium hydroxide aqueous solution (0.11 mol / L) was added to the slurry at the rate of 1.0mL/min using a metering pump for 8 hours. The obtained sedimentation was filtered and rinsed, and then dried at 60 degrees C for 1 day. About 20g powder was obtained.

[0045] X-ray diffraction pattern of this powder shows only peak of nickel hydroxide ($Ni(OH)_2$). The powder consists of spherical grain substantially shown in drawing 4 .



3

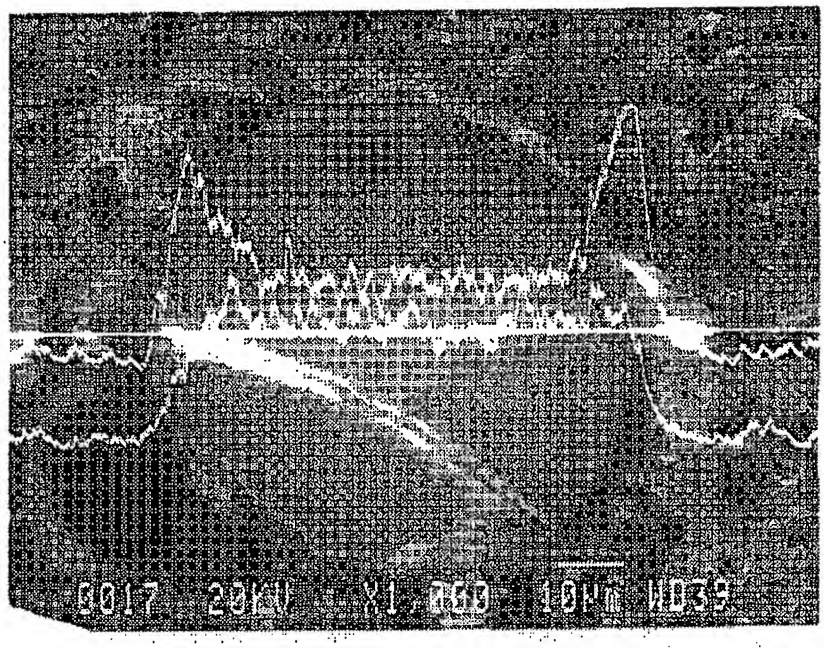
図面代用写真



4

[0046] EPMA (electron ray probe micro analyzer) result of the cross section of the particle is shown in drawing 5. It was observed that nickel and cobalt are unevenly distributed in the grain core and surface, respectively.

図面代用写真



5

[0047] From the above analysis results, it was confirmed that the core and surface of above-mentioned powder being spherical grain substantially consist of crystalline nickel hydroxide and amorphous cobalt hydroxide, respectively.

[0048] After mixing 4.2g of lithium-hydroxide monohydrates with 10.2g of this powder, it put into the crucible made of alumina, and calcinated at 800 degrees C for 10 h in oxygen ambient atmosphere, and black powder was obtained. It was found that this powder is the spherical particle of the two-layer structure and consists of lithium nickel multiple oxide (LiNiO2) in the core and lithium cobalt multiple oxide (LiCoO2) in the surface from X-ray diffraction, the line analysis of cobalt and nickel by EPMA, and SEM observation. Auger electron spectroscopy shows that the cobalt/(nickel + cobalt) atomic ratio is 0.2 or more until 0.1 um in depth from the grain surface.

[Table 1]

Surface

Core

cobalt/(nickel + cobalt)

実施例	表面層		中心層		表面層元素／中心層元素モル比
	元素	量（モル）	元素	量（モル）	
1	Co	0.02	Ni	0.2	0.1
2	Co	0.04	Ni	0.2	0.2
3	Co	0.08	Ni	0.2	0.4
4	Co Fe	0.072 0.008	Ni	0.2	0.4
5	Co	0.08	Ni Co	0.017 0.003	0.4
6	Co	0.06	Ni	0.2	0.3
7	Co	0.06	Ni	0.2	0.3
8	Co	0.02	Ni	0.2	0.1
9	Co	0.02	Ni	0.2	0.1
10	Co Cu	0.019 0.001	Ni	0.2	0.1
11	Co Mg	0.018 0.002	Ni	0.2	0.1
12	Co Al	0.019 0.001	Ni	0.2	0.1

[Table 2]

実施例	表面層		中心層		表面層元素／中心層元素モル比
	元素	量（モル）	元素	量（モル）	
13	Co Ti	0.016 0.004	Ni	0.2	0.1
14	Co	0.08	Ni V	0.017 0.003	0.4
15	Co	0.08	Ni Cr	0.017 0.003	0.4
16	Co	0.08	Ni Mn	0.017 0.003	0.4
17	Co	0.08	Ni La	0.017 0.003	0.4
18	Co Ni	0.017 0.003	Ni Ga	0.17 0.03	0.1
19	Co Zr Y	0.018 0.001 0.017	Ni Co Fe	0.16 0.03 0.01	0.1